THE
PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, Vol. 136, No. 5A 30 NOVEMBER 1964

Effect of Impurities on the Critical Temperature of Superconductors*

D. M. GINSBERG†
Department of Physics, University of Illinois, Urbana, Illinois
(Received 2 July 1964)

By extending the analysis of Markowitz and Kadanoff, it is shown that in homogeneous, low-concentration tin and indium alloys, impurity-induced changes in the critical temperature T_c, arising from all causes other than decreased anisotropy, can be convincingly analyzed into a part due to variations in the electron mean free path and a part due to variations in the number of conduction electrons. A comparison of the latter with direct measurements by Glover and Sherrill of the shift in T_c produced by electrically charging tin and indium films shows excellent agreement for five of the six alloy systems considered, although the sixth system shows poorer agreement. This analysis provides strong support for the theory of Markowitz and Kadanoff, and helps to separate the effect on T_c of changes in the phonon spectrum, the electron-electron coupling constant, and the electron density of states.

I. INTRODUCTION

IT has been shown theoretically by Markowitz and Kadanoff[1] that the change in a superconductor's critical temperature T_c produced by adding nonmagnetic impurities can be divided into two parts. One part results from the smoothing out of anisotropy which accompanies the shortened electron mean free path, and has been called the anisotropy effect. It was first predicted by Anderson,[2] and tends to lower the critical temperature as impurities are added, until the effect saturates when the mean free path has decreased to a value much smaller than the coherence length of the pure metal (typically, at a few percent impurity). The rest of the change in T_c is called the valence effect, and is expected to be approximately proportional to the amount of impurity added, at least for small amounts (a few percent). By comparing their theory with experimental data[3] for alloys of slightly doped tin, indium, and aluminum, Markowitz and Kadanoff (hereafter called M and K) were able to separate the contribution of the anisotropy effect from that of the valence effect. It should be noted that the names of these two effects may be misleading, since the difference between the valence of the impurity and that of the host helps to limit the electron mean free path, and since the valence effect is only partly related to this valence difference. In fact, the purpose of this paper is to show that one can convincingly divide the valence effect into two parts, one part (to be called the isotropic mean-free-path effect) inversely proportional to the electron mean free path, and another part (to be called the charge effect) proportional to the number of conduction electrons added to the metal. This should help open the way to a fundamental theoretical analysis of the valence effect.

We will restrict our attention to alloys in which the impurity is soluble at room temperature.[4] Although some of the samples considered by M and K were well annealed at temperatures at which the impurity was soluble, and were kept at room temperature for only a short time, experience shows that precipitation can occur very quickly.[5] This precipitation changes in an unknown way the electronic charge which each impurity atom contributes to the host, and makes impossible the kind of analysis we are trying to make. We will therefore examine only the data for alloys of tin doped with indium, cadmium, indium antimonide, and antimony, and for alloys of indium doped with bismuth, tin, lead, and thallium. (None of the aluminum alloys fulfill our solubility requirement.)

* Work supported in part by the National Science Foundation.
† Alfred P. Sloan Foundation Fellow.
[1] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).
[2] P. W. Anderson, Phys. Chem. Solids **11**, 26 (1959).
[3] E. A. Lynton, B. Serin, and M. Zucker, Phys. Chem. Solids **3**, 165 (1957); R. I. Gayley, Jr., E. A. Lynton, and B. Serin, Phys. Rev. **126**, 43 (1962); G. Chanin, E. A. Lynton, and B. Serin, *ibid.* **114**, 719 (1959); D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta Met. **9**, 861 (1961).
[4] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).
[5] See, for instance, J. D. Livingston, Phys. Rev. **129**, 1943 (1963).

In Sec. II, our method of analysis is described. In Secs. III and IV, we will treat the data for the tin and indium alloy systems, respectively. Section V contains a comparison of our results with experimental data obtained by Glover and Sherrill,[6] which provide direct values for the charge effect. We will find that the agreement is quite gratifying. Section VI contains a discussion of the possible further analysis of the isotropic mean free path effect and the charge effect.

II. METHOD OF ANALYSIS

The theoretical shift δT_c in the critical temperature is given[1] by

$$\delta T_c(\chi)=K^i\chi+\langle a^2\rangle T_c I_c(\chi), \quad (1)$$

where $\chi=(kT_c\tau_a)^{-1}$. K^i is a constant. It is expected to depend on both the type of impurity and the host metal. τ_a is defined by M and K's Eq. (41), and is essentially a mean time required for collisions to smooth out the anisotropy. (τ_a may not be the same as τ_{tr}, the appropriate relaxation time for transport processes.) $\langle a^2\rangle$ is the mean square anisotropy of the electron-electron coupling constant V, and $I_c(\chi)$ is a function which is defined precisely by M and K's Eq. (47), but which they show is conveniently approximated in the range of interest by the expression

$$I_c(\chi)\approx 0.078\chi\ln\chi-0.36\chi. \quad (2)$$

One expects χ to be proportional to the amount of impurity added, at least up to a few percent. The first term in Eq. (1) is the valence effect. The second term is the anisotropy effect.

In order to compare their theory with experimental results, M and K write the parameter χ in the form

$$\chi=\lambda^i\gamma\rho, \quad (3)$$

where λ^i is constant for a given host and impurity. (λ^i is the ratio τ_{tr}/τ_a of the two scattering times mentioned above.) γ is a collection of constants of the host metal, given by

$$\gamma=\hbar\bar{v}_F/(\rho lkT_c), \quad (4)$$

where $\bar{v}_F$ is the average Fermi velocity, l is the electron mean free path, k is Boltzmann's constant, and ρ is the residual resistivity of the alloy divided by the increase in resistivity which appears when the metal is heated up from 4° to 273°K. ρ is approximately proportional to $1/l$. Combining Eqs. (1), (2), and (3), we obtain a useful expression for δT_c:

$$\delta T_c=A\rho+B\rho\ln\rho, \quad (5)$$

where

$$A=\{K^i+\langle a^2\rangle T_c[-0.36+0.078\ln(\lambda^i\gamma)]\}\lambda^i\gamma \quad (6)$$

[6] R. E. Glover, III, and M. D. Sherrill, Phys. Rev. Letters 5, 248 (1960).

TABLE I. Parameters derived for the tin alloys.

Impurity	$K^i\lambda^i\gamma$ °K	ρ/n^i	δz	β °K	$\beta n^i\delta z/\alpha\rho$
In	0.53	0.058	−1	0.023	−0.43
Cd	0.68	0.14	−2	0.018	−0.27
InSb	0.93	0.060	0	...	...
Sb	1.24	0.059	1	0.018	0.33

and

$$B=0.078\langle a^2\rangle T_c\lambda^i\gamma. \quad (7)$$

[$(K^i\lambda^i\gamma)$ is the same as M and K's $(\partial T_c/\partial\rho)_0{}^i$.]

Our purpose, then, is to show that the valence effect, $K^i\lambda^i\gamma\rho$, can be written in the form

$$K^i\lambda^i\gamma\rho=\alpha\rho+\beta n^i\delta z, \quad (8)$$

where n^i is the percent impurity, δz is the difference between the impurity valence and the host valence, and where α and β are independent of the type of impurity, although they depend on the host metal. $\alpha\rho$ is the isotropic mean-free-path effect, and $\beta n^i\delta z$ is the charge effect.

III. ANALYSIS OF THE TIN ALLOY DATA

The parameter α which appears in Eq. (8) should be set equal to M and K's value of $K^i\lambda^i\gamma$ for InSb doping, since $\delta z=0$ for this impurity. Therefore $\alpha=0.93$°K for tin as the host metal.

The parameter β can now be found from Eq. (8). In this way we find the values for β listed in Table I, together with M and K's values for $K^i\lambda^i\gamma$, ρ/n^i, and δz, which are used in calculating β. The last column in Table I lists the ratio of the charge effect, $\beta n^i\delta z$, to the isotropic mean free path effect, $\alpha\rho$. It is seen that the former has a smaller magnitude than the latter, but that both contribute appreciably to the valence effect.

In light of the scatter in the experimental data (see M and K's Fig. 6), the agreement among the three values of β is perhaps as good as one could expect. This is an indication that the valence effect can indeed be written in the form of Eq. (8). In Sec. V we will see strong further evidence for this claim.

IV. ANALYSIS OF THE INDIUM ALLOY DATA

The analysis for the indium alloys is more complicated than for the tin alloys, because M and K show that λ^i is not approximately unity for all of the impurities added to indium, particularly for Tl doping, which we need to obtain α and begin the analysis. Their Table III gives values for $K^i\lambda^i\gamma$ which are nevertheless calculated by assuming $\lambda^i=1$ for all of the impurities. These values must now be corrected by using the values for λ^i listed in their Table V. The method of correction can be found as follows.

One takes the expression for δT_c in Eq. (5), with λ^i taken from their Table V and with their value $\lambda^i\langle a^2\rangle$

$=0.021$, and one sets it equal to a similar expression with $\lambda^i\langle a^2\rangle=0.021$ again, but with λ^i set equal to 1 and with their $K^i\lambda^i\gamma$. In this way, using their γ, which is 140, one finds that $K^i\lambda^i\gamma$ is to be corrected by the addition of $-0.078\times0.021\times T_c\gamma\ln\lambda_i=-0.782°\text{K}\times\ln\lambda^i$. From here on, the calculation proceeds in the same way as for the tin alloys.[7]

From the data for Tl doping, one finds that $\alpha=2.55°$K, and one then obtains the values for β which are listed in Table II. The last column shows that again both the isotropic mean-free-path effect and the charge effect contribute appreciably to the valence effect.

The agreement between β derived for Pb doping with that for Sn doping supports our claim of isolating a charge effect. The disagreement with β for Bi doping is an apparent contradiction of this claim. This will be discussed further in the next section.

V. COMPARISON WITH DIRECT MEASUREMENT OF THE CHARGE EFFECT

We have seen that for five of the six alloys we have discussed, we can isolate a charge effect. It is now imperative that we compare our results with the direct measurement of the charge effect. Glover and Sherrill[6] have determined the shift in T_c caused by charging thin films of these metals, thereby altering the electron concentration slightly. If our viewpoint is correct, our values for β should agree with their values for β', the change in T_c for each percent of an electron added per atom. They find that β' is 0.018°K for tin and -0.027°K for indium. These are in gratifying agreement with our values for β on all of our six alloy systems except the In-Bi alloys. This is a further indication that this alloy system does not fall into the desired pattern. The reason for this must await further investigation.[7a] Certainly the excellent agreement of β with β' for five of our six alloy systems can be nevertheless taken as convincing support for our analysis, and for the theory of M and K, from which we start. It should be noted that without the correction applied in Sec. IV to take into account the fact that $\lambda^i\neq1$ for the indium alloy systems, especially for the In-Tl alloys, β and β' disagree in sign. This provides evidence for M and K's conclusion that the two scattering times τ_a and τ_{tr} are not equal in the indium alloys.

TABLE II. Parameters derived for the indium alloys.

Impurity	$K^i\lambda^i\gamma$ °K	ρ/n^i	δz	β °K	$\beta n^i\delta z/\alpha\rho$
Bi	2.00	0.24	2	−0.066	−0.22
Sn	2.08	0.049	1	−0.023	−0.18
Pb	2.25	0.078	1	−0.023	−0.12
Tl	2.55	0.026	0	···	···

[7] The type of correction we have just made for the indium alloys is less necessary for the tin alloys, for which λ^i is close to 1 for each of the impurities. If one nevertheless wants to make this type of correction for the tin alloys, one can obtain values for λ^i from M and K's Table V again. There is no value listed for InSb. Consulting M and K's Fig. 6, we find the InSb points near those of Cd. Assuming, then, that a reasonable value of λ^i for InSb is 0.9, the same as for Cd, we find that our correction yields new values of β, which are 0.021, 0.017, and 0.021°K for In, Cd, and Sb impurities, respectively. For our purposes, these are essentially the same as those listed already in Table I, derived without the λ^i correction. (This correction for the tin alloys also changes α from 0.93 to 1.00°K.)

[7a] One possibility is that the bismuth atoms are not randomly distributed in the indium.

VI. DISCUSSION

We have succeeded in separating the valence effect into a part due to a variation in the mean free path and a part due to a variation in the number of conduction electrons. Our calculations have involved no adjustable parameters. We now go on to make some statements which are more speculative in nature.

It is not unreasonable to assume that the type of analysis we have made will also apply to many other homogeneous alloy systems. (For magnetic impurities, other effects will also be important.[2]) It may be of interest to briefly discuss these two contributions to the valence effect, although detailed analysis must await further theoretical investigation.

The valence effect is the change in T_c after the contribution from decreased anisotropy has been subtracted. The valence effect should therefore be interpretable from the original form of the BCS theory,[8] which was written in terms of an isotropic metal. According to this theory, the critical temperature is given by

$$kT_c=1.14\hbar\omega\exp[-1/(NV)], \tag{9}$$

where $\hbar\omega$ is some average phonon energy, N is the electron density of states at the Fermi surface in the normal metal, and V is the electron-electron coupling constant. Any contribution of the valence effect to δT_c must then result from variations in one or more of the three parameters ω, N, and V.

The charge effect may arise from changes in all three of these parameters.[9,10] The isotropic mean-free-path effect is expected to arise from changes in ω and V. Some idea of the influence of alloying on ω can be obtained from the specific heat data of Gayley, Lynton, and Serin.[11] An interpolation of their data shows that doping tin with 1% InSb or In lowers the Debye temperature by roughly 1%. It may be dangerous to assume from this result, which relates to long-wavelength phonons, that the short-wavelength phonons which are important for superconductivity[12] also have their frequencies lowered by 1%. However, if we do assume this, the lowering of ω changes T_c by about -0.04°K. Considering the InSb-doped tin now, to avoid a possible

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[9] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

[10] D. Pines, Phys. Rev. **109**, 280 (1958).

[11] See for instance R. I. Gayley, Jr., E. A. Lynton, and B. Serin, Phys. Rev. **126**, 43 (1962).

[12] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

charge effect, we need an *increase* in V of about 0.6% in order to bring the contribution of the isotropic mean-free-path effect to δT_c up to a value $\alpha\rho = 0.93°\text{K} \times 0.060 = 0.05°\text{K}$. (Gayley *et al.*[11] concluded from their data that alloying must increase V.)

Pippard[13] was apparently the first to consider the effect of decreased electron mean free path on V. He stated that this must always *decrease* V for an isotropic metal. However, he considered only longitudinal phonons in his analysis. The transverse phonons also contribute to V, and they would tend to *increase* V when the mean free path decreases.[14] It is possible that this problem will be clarified by further theoretical examination, taking proper account of the contribution of the different phonon modes, and including many-body effects.

In principle, the lattice parameter changes which accompany alloying can also influence ω, N, and V. However, these changes are so small[15] that one is not surprised that they can be ignored.

Since completion of this work, it has been pointed out to me by Dr. D. Markowitz that his Ph.D. thesis (University of Illinois, 1963, unpublished) contains a prior attempt to analyze the valence effect into a part proportional to $n^i\delta z$ and a part proportional to ρ, for the tin and aluminum alloys (not for the indium alloys). Our limitation of the discussion to alloys in which the solute is completely dissolved removes several of Dr. Markowitz's apparent exceptions to the hypothesis on which this analysis is based. Our comparison of the results of the analysis with measurements by Glover and Sherrill provides new support for this hypothesis. For a treatment of some of the physical mechanisms which are responsible for the charge effect and the isotropic mean free path effect, the reader is referred to Dr. Markowitz's thesis.

ACKNOWLEDGMENTS

I am grateful to L. P. Kadanoff for an interesting discussion of the fundamental processes contributing to the valence effect. A preprint sent me by M. H. Cohen, discussing the importance of the electron density in determining the properties of normal metals, helped to stimulate my thinking about the present problem.

[13] A. B. Pippard, Phys. Chem. Solids **3**, 175 (1957).
[14] A. B. Pippard, Phil. Mag. **46**, 1104 (1955).
[15] J. A. Lee and G. V. Raynor, Proc. Phys. Soc. (London) **B67**, 737 (1954). For the indium alloys, see the references in Hansen's book (Ref. 4).

PHYSICAL REVIEW VOLUME 136, NUMBER 5A 30 NOVEMBER 1964

Ultrasonic Attenuation in Superconductors Containing Magnetic Impurities‡

LEO P. KADANOFF* AND IGOR I. FALKO†
Department of Physics, University of Illinois, Urbana, Illinois

(Received 24 June 1964; revised manuscript received 13 July 1964)

The Abrikosov-Gor'kov theory for a superconductor with magnetic impurities is applied to the calculation of attenuation coefficients. In this calculation several electronic time-dependent correlation functions are evaluated, and these functions are then used to evaluate the attenuation. In the limit of low sound-wave frequencies, the resulting coefficients are expressed in terms of a single energy integral. The physical significance of the result is discussed in terms of an effective density of "normal electrons" and energy-dependent mean free paths. Then, the attenuation is evaluated in the limit of low temperatures for superconductors both with and without an energy gap.

I. INTRODUCTION

EXPERIMENTS on ultrasonic attenuation have proved to be a most useful way of gaining information about the nature of the superconducting state.[1] Because of experimental difficulties, mostly connected with sample preparation, these studies have hitherto been limited to superconductors which contain a negligible percentage of magnetic impurities. In this paper, we have attacked the problem of calculating the attenuation coefficients in materials containing larger percentages of magnetic impurities in the hope that our work might encourage future experimental work on these materials.

As Abrikosov and Gor'kov[2] first pointed out, superconductors with magnetic impurities are uniquely interesting because they have superconducting properties even in the absence of an energy gap. This behavior

‡ Supported in part by U. S. Army Research Office (Durham).

* Alfred P. Sloan Fellow.
† Present address: Physics Department, Universitet A. M. Gorkii, Kharkov, Ukraine, USSR.

[1] See, for example, J. R. Leibowitz, Phys. Rev. **133**, A84 (1964); R. Weber, Phys. Rev. **133**, A1487 (1964); E. R. Dobbs and J. M. Perz, Rev. Mod. Phys. **36**, 257 (1964); R. E. Love and R. W. Shaw, Rev. Mod. Phys. **36**, 260 (1964); P. A. Bezuglyi, A. A. Galkin, and A. P. Korolyuk, Zh. Eksperim. i Teor. Phys. (USSR) **39**, 7 (1960) [English transl.: Soviet Phys.—JETP **12**, 4 (1961)].

[2] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Phys. (USSR) **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].